



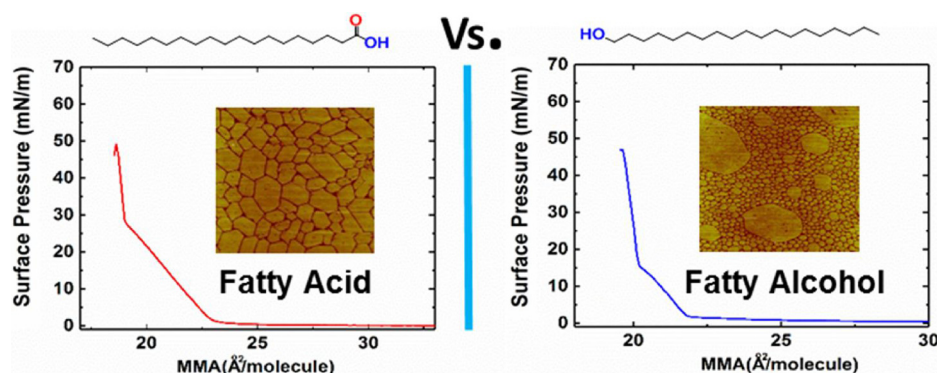
## The influence of surfactant head group on miscibility in mixed hydrocarbon-perfluorocarbon monolayers

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### GRAPHICAL ABSTRACT



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### ABSTRACT

Simple binary mixtures of hydrogenated and perfluorinated surfactants are typically immiscible in monolayers, with mixtures forming highly-structured films at the air-water and solid-air interfaces. While dispersion interactions between tail groups of the surfactants play a key role in dictating the micron-scale morphology of such mixed films, the influence of the head group on film morphology has been minimally explored. In this work, surfactant head group effects are investigated by comparing thermodynamic miscibility in combination with film morphology in binary mixed films comprised of nonadecanoic acid (ND;  $\text{CH}_3(\text{CH}_2)_{17}\text{COOH}$ ) with perfluorotetradecanoic acid (PF;  $\text{CF}_3(\text{CF}_2)_{12}\text{COOH}$ ), as well as the corresponding fatty alcohol nonadecanol (NDOH;  $\text{CH}_3(\text{CH}_2)_{18}\text{OH}$ ) with PF. Both the fatty acid and fatty alcohol were immiscible with PF in monolayers, with the systems exhibiting small, negative deviations from ideal mixing and forming phase-separated domains under a variety of preparation conditions. Micron and nanometer-scale film morphologies for the two sets of films were significantly different, however, with fatty acid mixtures tending to form polygonal, faceted domains enriched in hydrocarbon whereas the fatty alcohol mixtures formed significantly less structured domains, both at the solid- and liquid-air interfaces. Differences in film morphologies are discussed in terms of head and tail group interactions, and placed in context of existing literature on closely-related monolayer systems.

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## 1. Introduction

Fluorinated surfactants typically exhibit excellent surface tension lowering abilities, chemical stability and rapid spreading at the air-water interface, and often outperform their hydrogenated counter-parts in a variety of technological applications [1]. Fluorinated surfactants are frequently mixed with conventional hydrogenated surfactants to improve overall surface activity in various surfactant applications; for example, surfactant mixtures containing a fluorinated component are frequently used in fire-fighting foams, microemulsions and mixed micelles. Despite the varied and important uses of fluorocarbon-hydrocarbon surfactant mixtures, the mixing behaviour of these broad class of molecules is often non-ideal and quite complex because of the very different chemical properties of fluorocarbons and hydrocarbons. Simple fluorocarbon molecules are typically non-polarizable, mechanically inflexible and highly immiscible with water, whereas hydrocarbons are more polarizable, flexible but also immiscible with water. The two classes of compounds tend to be mutually immiscible, though for surfactants in aqueous systems, the presence of a polar head group adds further chemical complexities to their miscibility.

There have been significant recent research efforts aimed at understanding molecular-level factors which control miscibility in mixed surfactant systems, with an emphasis on using mixtures of hydrogenated and perfluorinated fatty acids in monolayers as simple, tractable model systems; various aspects of immiscibility and resulting film morphology in mixed surfactant systems have been reviewed, and readers are referred to these works for an overview of the field [2–4]. Mixed Langmuir or Langmuir Blodgett (LB) monolayer films comprised of simple hydrogenated and perfluorinated fatty acids are typically immiscible, with components undergoing phase-separation at solid and liquid-air interfaces. Immiscibility can broadly be attributed to a combination of the comparatively strong homomolecular dispersion interactions between hydrogenated surfactants and correspondingly weak homo- and heteromolecular dispersion interactions with the poorly-polarizable perfluorocarbons. However, subtleties in terms of the degree of immiscibility and the overall morphology of the resulting phase-separated film are highly-dependent upon the composition of the underlying liquid sub-phase (e.g. pH, ionic strength), the degree of film compression and more importantly, the precise chemical identity of the film components, including surfactants' tail group lengths and the identity of the head groups.

Much of our research group's work in this area has centred on correlating mixing thermodynamics and micron-scale film morphology with the surfactant tail length for compressed films (fatty acids in the untilted condensed phase). By keeping the headgroups fixed (carboxyl groups) and systematically varying the length of the alkyl fatty acid tail length, correlations between mixing properties and molecular structure can be made. These mixed systems are generally phase-separated, with repulsive, non-ideal interactions between film components, though variations in this exist. Our combined studies suggest a basic empirical relationship for phase-separation in these systems; in terms of film morphology, mixed systems in which the difference in tail length between the hydrogenated fatty acid and the perfluorinated fatty acid ( $\Delta_{H-F}$  = #CH<sub>2</sub> groups in hydrocarbon tail chain - #CF<sub>2</sub> groups in perfluorocarbon tail chain) are greater than six form micron-sized, phase-separated polygonal domains enriched in the hydrogenated component [5–7]. Decreasing  $\Delta_{H-F}$  favours formation of extended, line-like domains. These results can be broadly rationalized using McConnell's thermodynamic model developed for single-component monolayers [8], which invokes a competition between dipole-dipole repulsion between negatively-charged headgroups and line-tension between different phases; in the mixed system, altering the length of the alkyl tail under close-packing conditions enables tailoring of the line tension interaction and therefore the overall film morphology. Matsumoto et al. [9,10] have built upon this framework, through their investigations of phase-separated diblock fatty acids, and refined a model to describe

phase-separation in binary hydrocarbon-fluorocarbon systems which accounts for molecular-level interactions between the different functional groups on the surfactant tails.

We note that while these models are simple and provide an empirical, predictive ability for when systems will phase-separate and what the resulting gross film morphology will be, numerous subtle but important effects are lost. For example, domain growth kinetics [11] and solubility in the subphase [12] are known to affect phase-separation and morphology. Further, an important factor that has been minimally addressed in the literature is the chemical nature of the surfactant headgroup; the majority of studies to date have investigated fatty acids and the role played by the surfactant head group remains largely unexplored.

In this work, we have characterized the mixing thermodynamics and micron-scale domain structure of mixed monolayer films comprised of nonadecanoic acid (ND; CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>COOH) with perfluorotetradecanoic acid (PF; CF<sub>3</sub>(CF<sub>2</sub>)<sub>12</sub>COOH), as well as the corresponding fatty alcohol nonadecanol (NDOH; CH<sub>3</sub>(CH<sub>2</sub>)<sub>18</sub>OH) with PF. Based on the empirical predictive understanding described above, we hypothesized that the mixed ND:PF system ( $\Delta_{H-F}$  = +5) should form phase-separated, elongated polygonal domains comprised of ND dispersed in a PF matrix. For the subphase conditions typically used in our other works described above, the carboxyl head groups will be negatively charged giving a high density of negative charge at the air-water interface. In this work, replacing the carboxyl group with a simple, uncharged hydroxyl by using a fatty alcohol surfactant can reasonably be anticipated to influence dipole density and thus overall film morphology. This effect is explored in detail using a combination of thermodynamic mixing and film morphology measurements.

## 2. Materials and methods

### 2.1. Chemicals and substrates

Nonadecanol, nonadecanoic acid and perfluorotetradecanoic acid were purchased from Sigma-Aldrich and used as received. The solvents n-hexane and THF (ACS grade) were purchased from Fisher Chemicals and Sigma-Aldrich respectively, and used as received. Stock surfactant solutions were prepared by dissolving the solid surfactant in a 9:1 n-hexane:THF volume ratio to a desired molarity of  $2 \times 10^{-3}$  mol/L. Mixed surfactant solutions were prepared by mixing appropriate volumes of the surfactant solutions to obtain the desired mole fraction. The nomenclature XX:YY is used in the text to specify the mole fraction ratio of either NDOH:PF or ND:PF mixtures. Microscope slide cover glass (22 mm × 22 mm, VWR International) was used for LB deposition experiments. The cover glass substrates were sequentially rinsed with isopropanol, absolute ethanol and ultrapure water, dried with nitrogen, and finally treated with a plasma cleaner (Harrick Plasma) prior to film deposition.

### 2.2. Compression isotherms and Langmuir Blodgett (LB) film preparation

A commercial Langmuir trough system (KSV Instruments) with ultrapure water (18.2 MΩ cm, Millipore) as a subphase, was used in symmetric compression mode to collect surface pressure-area compression isotherms at a temperature of  $22 \pm 1$  °C. For compression isotherm measurements, the surfactant solution of interest was spotted onto a clean subphase surface using a Hamilton syringe. A period of at least ten minutes was allowed to ensure the evaporation of the solvent before compression. Surface pressures were measured with a platinum Wilhemy plate and isotherms were collected using a compression rate of  $7.0 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ . Isotherms were measured in triplicate to ensure reproducibility, and uncertainties in measured mean molecular areas were < 0.1% as determined by standard deviations in replicate measurements. LB deposition of surfactant films were carried out using the same apparatus and conditions as described above, but with a

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